Photoreversible Viscosity Changes and Gelation in Mixtures of Hydrophobically Modified Polyelectrolytes and Photosensitive Surfactants

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ABSTRACT: The viscosity and gelation of mixtures of hydrophobically modified poly(acrylic acid) (HM-PAA) and a cationic photosensitive surfactant can be controlled reversibly by changing between UV and visible light irradiation of the sample. At the critical aggregation concentration (cac) of the surfactant, micellar aggregates form on the polymer and solubilize the alkyl side chains grafted on the HM-PAA, leading to physical cross-linking and gelation. The hydrophobic trans (visible light) form, with a planar azobenzene group in the surfactant tail, has a lower cac than the more polar cis (UV light) form, resulting in gelation at lower surfactant concentrations under visible light. Reversible viscosity changes of up to 2 orders of magnitude are observed upon exposure to UV or visible light. Observed viscosity maxima of 5.6×10^4 cPa for the trans form and 2.2×10^3 cPa for the cis form of the surfactant suggest that the trans-form surfactant micelles are more effective at solubilizing the alkyl side chains than are the more hydrophilic cis-form micelles. Steady-state fluorescence studies of the cationic probe crystal violet reveal an enhancement in binding of the crystal violet to sites adjacent to bound surfactant molecules as the surfactant concentration is initially increased prior to the cac, followed by a decrease in binding of crystal violet at concentrations above the cac due to a decrease in the number of available binding sites as the anionic polyelectrolyte wraps around the newly formed cationic micelles. The nearest-neighbor binding is greater in the trans form as opposed to the cis. Surface tension values decrease slowly with increasing surfactant concentration below the cac due to strong binding of the surfactant to the polyelectrolyte, followed by a large drop in the surface tension at the cac that results from release of bound surfactant upon micelle formation and subsequent wrapping of the surfactant aggregates by the polyelectrolyte. Dynamic viscoelastic measurements are typical of gel systems with $G' > G''$ above the cac and also indicate that approximately 25% of the polymer chains are elastically effective in the presence of the trans form, while only 7.5% of polymer chains participate in cross-linking in the presence of the cis form of the surfactant.

Introduction

The interactions of polymers with surfactants exhibiting unique synergistic properties have received considerable attention over the past several decades and are the subject of many excellent reviews.[1−8] One of the most important features of such polymer−surfactant systems is the binding of the surfactant onto either the hydrophilic or the lipophilic portions of the polymer through electrostatic or hydrophobic interactions. This often allows for the properties of the resulting polymer−surfactant complex to be controlled easily by factors such as temperature, pH, and ionic strength in a far more efficient manner than through the molecular engineering of new polymers capable of exhibiting a similar responsiveness.

A special subset of polymer−surfactant systems involves the interactions of ionic surfactants with oppositely charged polyelectrolytes that, through either hydrophobic modification or some natural structural coincidence, contain lipophilic side chains along the polymer backbone. In this case, a high degree of binding is observed, and mixed micelles often form between the surfactant and side chains at concentrations well below the critical micelle concentration (cmc) of the pure surfactant system. Specifically, surfactant binding to hydrophobically modified polymers generally occurs in three stages.[9] In the solubilization stage at low amounts of surfactant, increasing the surfactant concentration results in a slow increase in the amount of bound surfactant, with this surfactant potentially becoming solubilized in intramolecular micelles that, depending on the hydrophobically modified fraction and ionic strength, may exist in the polyelectrolyte solution as a result of the hydrophobic nature of the side chains. At high surfactant concentrations, however, cooperative binding results in a rapid increase in the amount of bound surfactant, where the properties of the mixed surfactant side chain micelles become increasingly like those of pure surfactant micelles. Intermediate between these two stages exists a relatively broad region of transition from single-molecule solubilization to cooperative binding, generally occurring near the point where the amount of bound surfactant equals the number of hydrophilic side chains.

The onset of cooperative binding is often termed the "critical aggregation concentration" (cac), a convention originating from early studies of surfactant binding to polymers that did not contain hydrophobic side groups.[10] In these studies, very little binding of the surfactant to the polymer occurred until a critical surfactant concentration was reached (i.e., the cac). For hydrophobically modified polymers, however, binding results from both electrostatic interactions between the polyelectrolyte and the surfactant molecules as well as hydrophobic interactions between the lipophilic side chains of the graft copolymer and the surfactant tails. Thus, even

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though some degree of modest surfactant binding does occur in the solubilization region prior to cooperative binding, the general convention is to equate the cac to the initiation of cooperative binding as it provides a convenient means of denoting the origin of the rapid formation of micelles capable of simultaneously solubilizing side chains from different polymer molecules and thereby forming cross-links responsible for gelation. The difficulty in determining the onset of cooperative binding, and, consequently, in defining the cac precisely, has been demonstrated in mixtures of hydrophobically modified poly(acrylic acid) (HM-PAA) with cationic surfactants where gradual increases in solution viscosity[11] or gradual decreases in the I_1/I_3 value of solubilized pyrene[12] (which indicate the formation of hydrophobic surfactant side chain domains) prior to gelation and true (i.e., rapid) cooperative binding have been observed.

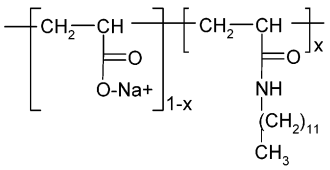
Surfactants with azobenzene structural units in the lipophilic tail offer the ability to control uniquely interfacial properties through irradiation with light of appropriate wavelengths.[13−17] The planar trans (visible light) form of such surfactants is more hydrophobic than the nonplanar cis (UV light) form, and hence the cmc, which typically correlates with the hydrophobicity of the surfactant tails,[18−23] is lower for the trans than the cis isomer of the surfactant.[13] Therefore, it may be possible under visible light irradiation for trans surfactant molecules to aggregate on the polymer and induce cross-linking and gelation at concentrations where the more hydrophilic cis surfactant molecules exhibit a lesser extent of aggregation onto the polymer to provide little or no cross-linking of the polymer chains. Irradiation of the trans-form micelles with UV light should cause the surfactants to adopt the more hydrophilic cis form, with a subsequent dissolution of the micelles and a breaking up or weakening of the gel structure. Thus, it is possible to envision photoreversible gelation in systems containing appropriate azobenzene surfactants and, for instance, hydrophobically modified polyelectrolytes such as HM-PAA. Similar photoresponsive viscosity changes and photoresponsive phase transitions have been achieved by incorporating azobenzene or other light-sensitive moieties directly in the polymer chain, either in the backbone or as pendant groups.[24−36] The strategy suggested here for the development of photostimulated gels would appear to be more versatile in some respects as it does not require extensive polymer synthesis for optimization of properties; rather, the photogelation properties can be tuned by varying surfactant concentration and structure. Such photoreversible gels could be used for a range of applications, including surface patterning using optical grids to generate periodic gelled regions, optical traps whereby nanoparticles and/or proteins would be localized within viscosity wells, low pressure-drop separations utilizing a moving high-viscosity wave front to achieve separation based on size rather than particle flow or diffusion, and novel microfluidic applications where a complex system of low-viscosity channels could easily be etched in gelled layers with lasers or optical stencils.

Although the cis and trans forms of azobenzene surfactants have different cmc values, it remains to be seen whether this will correspond to a difference in cac values and, thus, allow photocontrol over the gelation properties of azobenzene surfactant/HM-PAA solutions. The reason for this uncertainty is that the driving force for aggregation of surfactant molecules onto the polymer is quite complex. On one hand, gelation in mixtures of anionic HM-PAA and the cationic dodecyltrimethylammonium bromide (DTAB) surfactant is greater than in the case of nonionic $C_{12}E_5$ and anionic sodium dodecyl sulfate (SDS) surfactants,[11] suggesting that the electrostatic attractions between the polyelectrolyte and the surfactant play an important role. On the other hand, gelation in mixtures of fluorocarbon-modified polyelectrolytes, i.e., polyelectrolytes with fluorocarbon side chains as opposed to the alkyl side chains of polymers such as HM-PAA, is observed to be stronger than in the case of the hydrocarbon counterparts.[37,38] Since fluorocarbons are more hydrophobic than hydrocarbons, this suggests that hydrophobicity may be the dominant effect controlling gelation in HM-PAA/surfactant mixtures. Similar effects of increased hydrophobicity on gelation have been observed through the use of longer hydrocarbon side chains.[11,12,39]

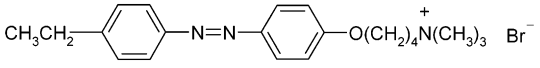
In the present study, we investigate cationic azobenzene surfactant aggregation in the presence of hydrophobically modified poly(acrylic acid) (2.5 wt %) as a means to impart photoreversible viscosity changes. The ability of the surfactant aggregates to act as cross-linkers by solubilizing the alkyl side chains of the polymers is studied with low-shear viscosity measurements, allowing for determination of the critical aggregation concentration (cac) of the trans and cis forms of the surfactant. Further dynamic viscoelastic measurements are used to provide evidence of gelation as well as to estimate the percentage of polymer chains that act as bridges between surfactant micelles. The fluorescence of the cationic probe crystal violet is then used to investigate the binding of surfactant molecules to the polymer both below and above the cac as the surfactant concentration is increased. Surface tension measurements are used to investigate the interaction of the surfactant with the polymer and to provide independent verification of the cac measurements. Finally, the results for the trans and cis forms of the surfactant are compared and examined in terms of solubilization efficiency and micelle hydrophobicity. The experimental results are consistent with the picture that binding and aggregation of the surfactant to the polymer at the cac is responsible for the polymer cross-linking and gelation.

Experimental Section

Materials. Hydrophobically modified poly(acrylic acid) (HM-PAA) of the form



was synthesized by reaction of the acid form of the polymer (MW = 250K g/mol) with dodecylamine in the presence of 1,3-dicyclohexylcarbodiimide in the anhydrous solvent 1-methyl-2-pyrrolidinone.[40] The degree of conversion, as determined by ^{1}H NMR from the relative sizes of the CH_3 and CH peaks, was $x = 3\%$. The azobenzene−trimethylammonium bromide surfactant (azoTAB) of the form



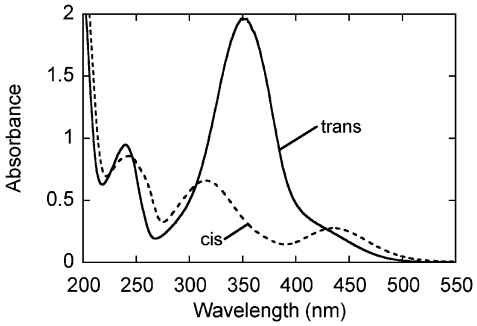


Figure 1. UV−vis spectra of 0.43 mM azoTAB solutions obtained using a 0.2 cm path length cell.

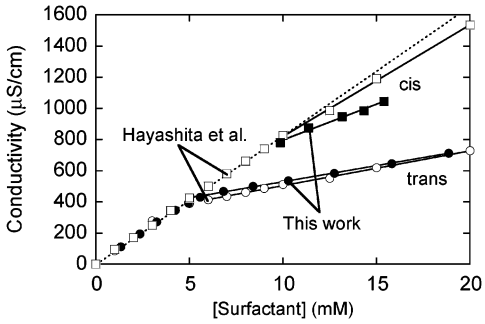


Figure 2. Conductivity data for pure solutions of azoTAB at 25 °C compared to literature values.[13]

was synthesized according to published procedures,[13,17] with a purity of 99% as determined by GC and NMR. All materials were obtained from Aldrich in the highest purity available.

Trans and Cis Conversions. The UV−vis spectra of the trans and cis forms of the azoTAB surfactant are shown in Figure 1. The absorbance peak centered at 350 nm for the trans form corresponds to the wavelength of light responsible for conversion to the cis (UV light) form. Similarly, the absorbance peak centered at 435 nm for the cis form corresponds to the wavelength of light responsible for conversion to the trans (visible light) form. For conversion from the trans form to the cis form, solutions were stirred while being irradiated with light from a 200 W mercury lamp equipped with a 320 nm band-pass filter (Oriel, model no. 59800), while a 400 nm long-pass filter (Oriel, model no. 59472) was used for conversion from the cis to the trans form. A heat-absorbing filter (Oriel, model no. 59042) was placed in the beam path to absorb the IR light produced by the lamp. Auxiliary UV−vis experiments (not shown) proved that 1 h of irradiation (with stirring if possible) was more than sufficient to achieve full conversion, despite the relatively large extinction coefficients of the azoTAB surfactant (at λ_{max}, $\epsilon_{trans} = 22.9$ mM^{-1} cm^{-1} and $\epsilon_{cis} = 3.22$ mM^{-1} cm^{-1}). Deconvolution of the spectra revealed that the trans surfactant spectra consistently exhibited a cis shoulder peak with a height of about 8% (±0.5%) of the trans peak, consistent with the photostationary equilibrium between the two surfactant forms under visible light. For the cis surfactant a similar equilibrium amount of the trans form is expected; however, it was not possible to deconvolute the trans peak at 350 nm due to the secondary cis peak at 315 nm (see Figure 1).

The trans ↔ cis conversion is completely reversible.[17] Since the trans form has a slightly lower energy than the cis form of the surfactant, however, there is a slow rate of thermal conversion of the cis form to the trans form following irradiation, even in complete darkness.[41−43] Auxiliary experiments (not shown) demonstrated that thermal conversion led to an appreciable change in the cis-to-trans ratio only after several hours. Consequently, all experiments performed on the cis form of the surfactant were typically completed within 1 h, where the thermal conversion was small (<5%).

Viscosity Measurements. Viscosity measurements were performed with a cone-and-plate rheometer (AR-1000-N, TA Instruments) using a 4° cone with a diameter of 4 cm. The reported viscosities were the low-shear (0.02−1 s^{-1}) Newtonian viscosities measured at 25 °C. For measurements with the cis form of the surfactant, the solution was loaded in near-dark conditions, and the viscometer was covered to prevent conversion to the trans form by ambient light. The viscosity measurements were completed within 30 min of loading to prevent thermal conversion to the trans form.

Fluorescence and Absorbance Measurements. Fluorescence measurements of the cationic probe crystal violet were performed on a TimeMaster fluorescence lifetime spectrometer (Photon Technology International) in steady-state mode at 25 °C. Since the quantum yield of crystal violet is low in aqueous solutions with low viscosity (see Results and Discussion), an average of 10 scans at each wavelength was used to produce a satisfactory signal-to-noise ratio, S/N. The resulting scan times of approximately 35 min were therefore well within the range where thermal conversion was insignificant, and conversion from cis → trans due to the excitation beam was found to be less than 2%. A crystal violet concentration of 3.4×10^{-6} M was used with an excitation wavelength of 590 nm. The slit widths for excitation and emission were 1 and 2 nm, respectively. Absorption measurements were obtained with an HP 4853 UV−vis spectrophotometer using cells with a path length of 1 cm.

Surface Tension Measurements. Surface tension measurements were performed using a Krüss K-10 tensiometer equipped with a platinum Wilhelmy plate at 25 °C. For solutions with the cis form of the surfactant, the windows of the tensiometer were covered after loading to prevent room light from impacting the sample. In all cases, the surface tension was allowed to maintain an equilibrium value for at least 30 min before recording. For most surfactant concentrations, the equilibrium value was reached after about 10 min; however, for low surfactant concentrations (0.083 mM) upward of a few hours was required. UV−vis examination of the solutions following surface tension measurements indicated that thermal conversion was negligible.

Results and Discussion

Pure Surfactant Solutions. Conductivity data for solutions of the trans and cis forms of the azoTAB surfactant are shown in Figure 2 and compared to literature data.[13] A distinct break point in each conductivity curve is evident at the critical micelle concentration (cmc), i.e., the concentration at which micelles first begin to form. Below the cmc, the increase in molecularly dissolved azoTAB results in a relatively steep increase in the solution conductivity with surfactant concentration. Above the cmc, however, additional surfactant is incorporated into aggregates (micelles). These aggregates are large relative to individual surfactant molecules, and a substantial fraction of the counterions are condensed on the surface of the micelles. Thus, the conductivity increases at a lower rate with increasing surfactant concentration than below the cmc, resulting in the change of slope at the cmc.

The cmc of the trans-form surfactant is about 5.3 mM, while that of the cis-form is approximately 9.5 mM. This reflects the difference in hydrophobicity of the trans and cis forms because, with all else being equivalent, surfactants with more hydrophobic (i.e., less water-soluble) tails tend to form micelles at lower surfactant concentrations than surfactants that are less hydrophobic.[18−23] Since the cis form of the azobenzene group exhibits a larger dipole moment (3.1 D) across the azo linkage compared to the trans surfactant (0.5 D),[17] the cis form is less hydrophobic and, hence, has a greater cmc value than the trans form. Additionally, the data are in excellent agreement with those of Hayashita et al.,[13] with modest discrepancies at higher concentrations.

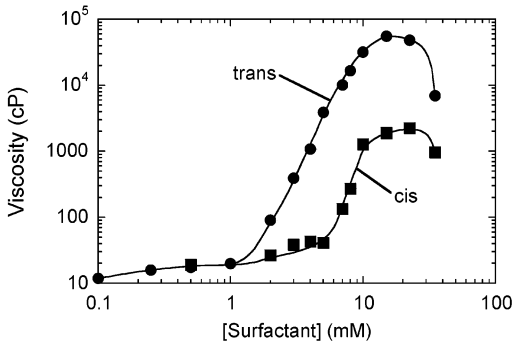


Figure 3. Low-shear viscosity of 2.5 wt % HM-PAA solutions as a function of azoTAB surfactant concentration under initial exposure to visible light (●), followed by exposure to UV light (■).

Viscosity of AzoTAB/HM-PAA Solutions. Viscosity measurements for the trans and cis forms of the azoTAB surfactant in the presence of 2.5 wt % HM-PAA are shown in Figure 3. In both cases, increases in the surfactant concentration initially result in a modest increase in viscosity. At some characteristic surfactant concentration for both the trans and cis forms, however, a sharp increase in solution viscosity is observed. In mixtures of DTAB and HM-PAA, this breakpoint was found to coincide with the onset of cooperative binding of the surfactant to the polymer and was thus termed the cac.[11] At this point we can conjecture (and in the subsequent sections show) that the sharp rise in the solution viscosity with surfactant concentration is a result of the rapid formation of surfactant aggregates on the polymer due to cooperative binding that are capable of solubilizing the alkyl side chains, resulting in physical cross-linking of the polymer chains and gelation, as shown in Figure 4. From the intercept of linear fits of the solution viscosity vs surfactant concentration (on a log−log scale) both above and below the breakpoint, the cac of the trans and cis forms of the surfactant can be estimated to be 1.4 and 6.1 mM, respectively. Note that the hydrophobic trans form has a lower cac than the more hydrophilic cis form, similar to decreases in cac values observed upon increasing the carbon number of traditional surfactants,[44,45] suggesting that hydrophobic effects are an important factor governing the aggregation of the surfactant micelles on the polymer chains. Since the trans and cis forms of azoTAB have different apparent cac values, it is possible to achieve relatively large changes in the solution viscosity through exposure to the appropriate wavelength of light. At a surfactant concentration of 5 mM, for example, a 2 orders of magnitude change in the viscosity is observable upon switching between the trans and cis forms. This viscosity swing was observed to be completely reversible, with only a few minutes in general required to decrease the viscosity during the trans → cis conversion. Conversely, while an initially rapid rise in the viscosity occurred within a few minutes of reexposure to visible light during the cis → trans conversion, returning to the equilibrium visible light value required longer times (on the order of 24 h). For example, at a surfactant concentration of 5 mM, 4 min of exposure to UV light was sufficient to decrease the viscosity to the equilibrium cis value shown in Figure 3. Upon reexposure to visible light, about 50% of the original trans viscosity value was recovered in about 4 min, while a longer "curing time" of about 24 h was necessary to fully return to the equilibrium trans value.

With further increases in the surfactant concentration beyond the cac, the viscosity eventually passes through a maximum and then decreases, consistent with the idea that as more micelles are formed, the number of alkyl side chains per micelle decreases, and the effectiveness of micelles to act as cross-linkers diminishes. The concentrations at which the maximum in viscosity occurs for the trans and cis forms of azoTAB are offset by a value similar to the difference in the cac values of the two forms, suggesting equivalent side chain-to-micelle ratios for both the trans and cis forms. Indeed, "dissolution" of the mixed micelles formed between surfactant molecules and side chains upon increasing the surfactant concentration is generally expected to occur at β = [bound surfactant]/[side chain] ≥ 1,[9] where the nature of the micelles becomes dominated by the surfactant, and it becomes less probable that an individual micelle will contain side chains from two or more

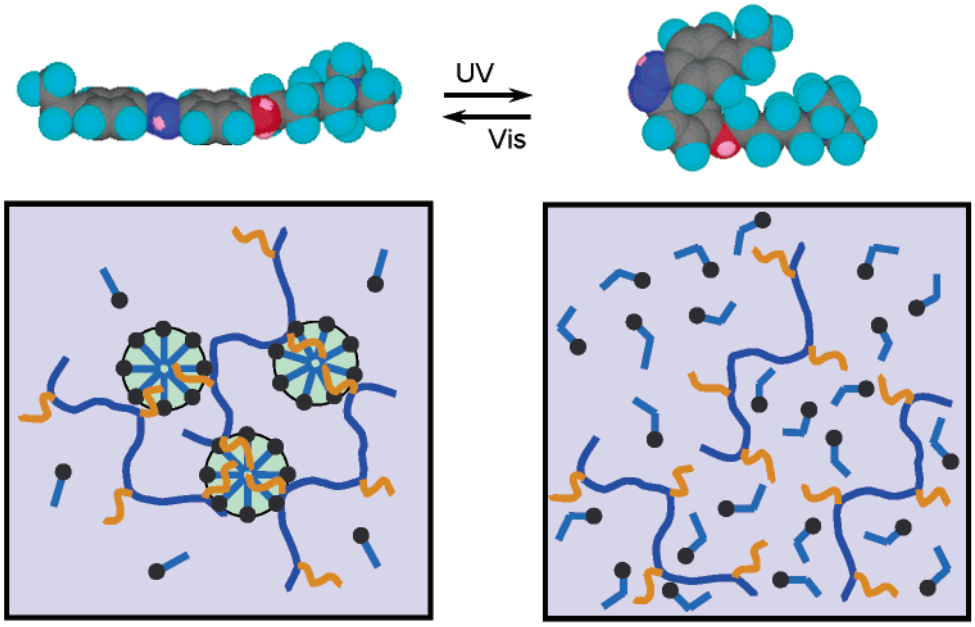


Figure 4. Illustration of the proposed mechanism of reversible gelation with light.

polymers. In mixtures of HM-PAA, the concentration of free (i.e., unbound) azoTAB surfactant in Figure 3 is expected to be quite low, and thus, the β values at maximum viscosity can be estimated from the overall surfactant concentration to be 1.4 and 2.0 for the trans and cis surfactants, respectively, consistent with the dissolution criterion above.

The maximum viscosity obtained for the trans form is significantly higher than that for the cis, implying that the trans micelles may be more effective at forming mixed micelles via solubilization of the alkyl side chains (thus, acting as cross-linkers) than the cis micelles. A comparison of the cis and trans conformations of the surfactant shown in Figure 4 reveals a likely explanation for this difference. In the trans form of the surfactant, the azobenzene group is nearly planar, resulting in relatively extended conformations of the surfactant tails. In the cis form, however, the two phenyl rings of the azobenzene group are folded upon each other, giving rise to a much more compact surfactant tail. Indeed, the bulky nature of the cis surfactant results in smaller micelles both in pure surfactant solutions and in mixtures with HM-PAA ($R_{g,cis} \sim 14$ Å vs $R_{g,trans} = 22$ Å in both cases),[46] consistent with the observation that for spherical micelles the diameter is approximately twice the surfactant length. Furthermore, since solubilization[47] and mixed micelle formation[48,49] are often optimum when the surfactant and secondary component have hydrocarbon chains of similar lengths, the lower effectiveness of gelation for the cis surfactant observed in Figure 3 is expected considering that the C_{12} side chains are closer in length to the extended trans form of azoTAB.

At surfactant concentrations greater than about 50 mM, it became impossible to simultaneously solubilize azoTAB and HM-PAA in a one-phase mixture. This limiting concentration of about 50 mM in the 2.5 wt % polymer solution ([surfactant]/[COO^-] = 19.8%) compares well with published values for mixtures of DTAB and HM-PAA of varying type and degree of substitution. For 1.0 wt % polymer solutions in water, the limiting surfactant concentration that resulted in a one-phase mixture was observed to be about 20 mM ([surfactant]/[COO^-] = 20.1%), independent of the amount (1%−3%) or type (C_{12} or C_{18}) of side chains.[11,12] It appears, therefore, that phase separation is a result of electrostatic and not hydrophobic interactions and is likely due to neutralization of the polymer−surfactant complex.

Fluorescence and Absorbance of Crystal Violet. The cationic fluorescence probe crystal violet was used to more closely study the binding of the cationic azoTAB surfactant to the anionic HM-PAA. Crystal violet is a well-known "microviscosity" probe with a fluorescence emission that decreases dramatically with the relative ease of the rotational relaxation of the aromatic rings. Thus, the fluorescence emission of crystal violet in glycerol is nearly 3 orders of magnitude greater than in water[50] and nearly 2 orders of magnitude larger when bound to polyelectrolytes or proteins, both of which give rise to a steric hindrance for this rotational relaxation.[51] The excitation peak of crystal violet ($\lambda_{max} = 590$ nm in water) allows this probe to be studied readily in concentrated azoTAB solutions without conversion of the cis → trans form (see Figure 1). Additionally, crystal violet acts as a polarity indicator, with λ_{max} shifting from the aforementioned 590 nm in water to 605 nm in benzene.[52] Thus, information on the degree and site of binding can be obtained for crystal violet and inferred for azoTAB by examining the fluorescence and λ_{max} of crystal violet in azoTAB/HM-PAA solutions.

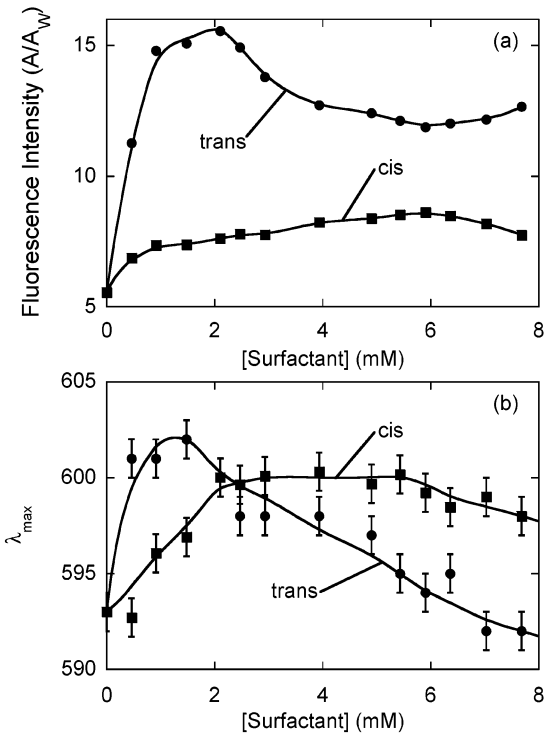


Figure 5. (a) Fluorescence emission of crystal violet ($\lambda_{excite} =$ 590 nm) normalized to the fluorescence in pure water and (b) the wavelength of maximum absorption of crystal violet in 2.5 wt % HM-PAA solutions as a function of added surfactant.

Figure 5 shows the normalized fluorescence emission and λ_{max} of crystal violet in 2.5 wt % HM-PAA solutions containing either the trans or the cis form of azoTAB. Without the addition of surfactant, the fluorescence emission of crystal violet was 5-fold higher in the presence of HM-PAA than in pure water, with an absorption maximum just slightly higher than observed in pure water. This suggests that there was a significant degree of binding of crystal violet to the HM-PAA, with the probe experiencing a slightly less polar environment. As the trans-form surfactant concentration increased, an initial large increase in the fluorescence emission and absorption maximum was followed by a leveling off and then decrease in these properties at successively higher surfactant concentrations. The initial increase in fluorescence emission with surfactant concentration suggests a nearest-neighbor type of binding phenomenon, where binding of the azoTAB results in a greater fraction of crystal violet binding to the polymer at sites adjacent to the bound surfactant. This is supported by the concurrent initial increase in the absorption maximum of crystal violet with surfactant concentration, which implies that the azobenzene groups of azoTAB provide a low-polarity environment for crystal violet (compared to water), similar to that of benzene. The peaks in both the fluorescence emission and λ_{max} for the trans-form azoTAB begin to decrease at ca. 2 mM, similar to the value estimated as the cac from Figure 3. An oppositely charged polyelectrolyte will wrap around the surfaces of the newly formed micelles,[44,45,53] since the micelles behave essentially as large, multivalent counterions for the polyelectrolyte and provide an increased driving force for the polyelectrolyte binding. The micelle, thus, occupies many of the binding sites

on the polymer, causing a release of single-species counterions (in this case Na^+) and other bound molecules.[54,55] Thus, the decrease in the fluorescence emission and λ_{max} of crystal violet above the cac is consistent with the onset of rapid cooperative binding of the surfactant into the mixed C_{12}-azoTAB micelles, which would cause the surface of the micelles to exhibit increased cationic character, thereby causing the polyelectrolyte molecules to wrap around the micelles, leading to release of crystal violet into the bulk water phase. Note that although the azoTAB molecules are slowly solubilized in the C_{12} micelles as the surfactant concentration is increased prior to the cac, it is not until cooperative binding gives rise to a dramatic increase in the amount of bound azoTAB molecules that a release of crystal violet back into the water phase is observed.

Further increases in the concentration of the trans-form azoTAB beyond the cac of ca. 2 mM result in a steady decrease in the λ_{max} of crystal violet, back to a value consistent with a high polarity (i.e., water) environment. However, the fluorescence emission at first decreases and then begins to increase at surfactant concentrations higher than about 6 mM. Note that the fluorescence emission *and* adsorption maximum of crystal violet both increase dramatically at the cmc in pure trans surfactant solutions (data not shown),[46] since crystal violet becomes preferentially solubilized in the low-polarity, but relatively high-viscosity, micelle core.[56−60] Thus, it is unlikely that free micelle formation at the cmc = 5.3 mM is responsible for the increase in the fluorescence emission seen at 6 mM in the trans-form azoTAB/HM-PAA solutions. One explanation is the formation of crystal violet dimers at higher surfactant concentrations[61] due to a reduction in the electrostatic repulsion between crystal violet molecules.[62]

The fluorescence emission and λ_{max} of the cis azoTAB in azoTAB/HM-PAA solutions behave similarly to the trans form, albeit to a weaker extent (see Figure 5). Increasing the cis surfactant concentration causes the fluorescence emission initially to increase and then to go through a broad maximum, followed by a decrease at surfactant concentrations higher than about 6 mM. This decrease occurs close to the cac = 6.1 mM of the cis form estimated from Figure 3 and provides further evidence of the cooperative binding process that results in rapid micelle formation beyond the cac. The arguments for this case are the same as for the trans case, namely that at the cac the polymer envelops the newly formed and increasingly cationic micelles, causing release of bound species. The degree of crystal violet-to-azoTAB nearest-neighbor binding on HM-PAA prior the cac appears to be less in the cis case than in the trans, likely a result of the increased hydrophilicity of the azobenzene group in the cis state. In addition, the mixed micelles formed between the compact cis-form azoTAB and the C_{12} side chains are expected to be rather ill-formed considering the severe packing constraints imposed upon a system with two species of dissimilar tail lengths, as discussed above. Furthermore, analysis of neutron-scattering data using a rescaled mean spherical approximation (MSA) for Coulombic interactions[63−65] suggests that the surfaces of cis azoTAB micelles have a lower net charge than the trans counterparts,[46] likely resulting from the migration of cis −N=N− groups, which are relatively hydrophilic due to an increase in the dipole moment in the cis (nonplanar) state, to the micelle interface. This decrease in net surface charge of the micelles would result in a decrease in the driving force that causes the polyelectrolyte to wrap around the micelle interface. Together, these phenomena explain why the cac is less well-defined for the cis form as opposed the trans form in Figure 5.

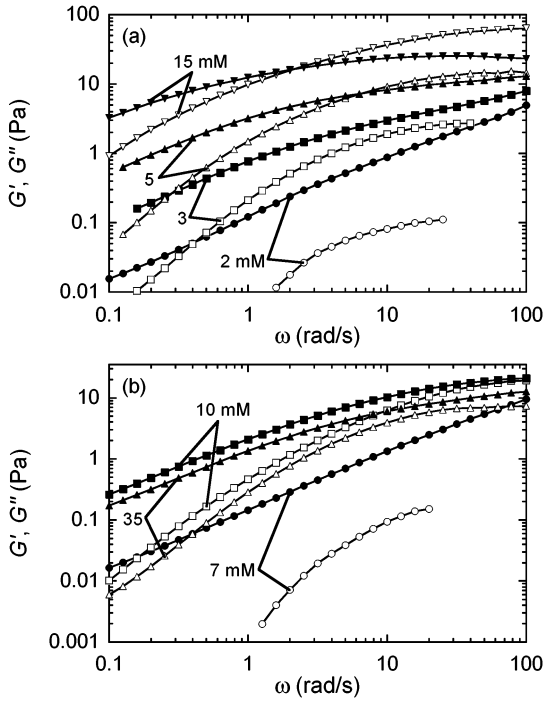


Figure 6. Dynamic viscoelastic behavior of 2.5 wt % HM-PAA solutions as a function of the amount of added (a) trans and (b) cis surfactant. G', open symbols; G'', closed symbols.

Dynamic Viscoelastic Measurements. The dependence of the storage modulus (G') and the loss modulus (G'') on angular frequency (ω) for HM-PAA/azoTAB mixtures is presented in Figure 6 for a few representative surfactant concentrations. At surfactant concentrations below the cac, $G'' > G'$ throughout the entire frequency range. As the cac of each form of the surfactant is surpassed, however, the dynamic viscoelastic response becomes typical of gels with G' becoming greater than G'' above a characteristic crossover frequency. For both the trans and cis forms of the surfactant, the initial concentration at which the high-frequency G' is observed to be greater than G'' is slightly larger than the corresponding cac, namely between 3 and 5 mM for the trans form (cac ≅ 2 mM) and ca. 10 mM for the cis form (cac ≅ 6 mM). This indicates that a sufficient number of cross-linkers, i.e., micelles, need to be generated before gellike properties are realized.

From the value of G' at large (i.e., "infinite") frequency (i.e., G_∞), we can estimate the fraction of elastically effective chains[66−69] by noting that $G_\infty = \nu_{eff}RT$, with ν_{eff} being the molar density of chains that act as bridges between two cross-linkers (i.e., elastically effective chains connecting two junctions, not loops or dangling ends), where uncertainties such as chain polydispersity and heterogeneity of the cross-linkers are neglected. The quantity G_∞/NRT (N = total molar concentration of polymer chains) is then the fraction of elastically effective chains, displayed in Figure 7 as a function of the amount of trans and cis surfactant added to HM-PAA solutions. The fraction of chains participating in cross-linking is seen to be effectively zero at low surfactant concentrations but then increases sharply at

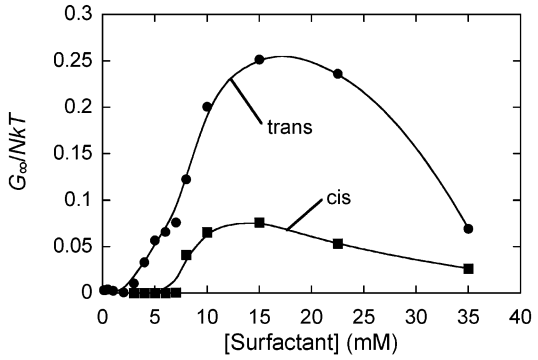


Figure 7. Fraction of elastically effective chains in 2.5 wt % HM-PAA solutions as a function of the amount of added surfactant.

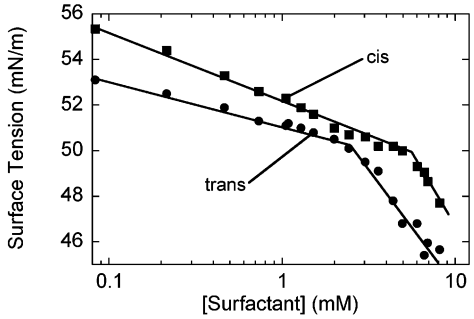


Figure 8. Surface tension of dilute (0.25 wt %) HM-PAA solutions as a function of surfactant concentration.

about 3 mM for the trans form and 8 mM for the cis form of the surfactant. Again, these values are slightly larger than the cac values determined previously (2 and 6 mM, respectively), consistent with the view that a prerequisite number of cross-linkers is required to achieve gelation. Further note that the maximum number of elastically effective chains is about 25% in the presence of the trans form of the surfactant compared to a maximum of around 7.5% with the cis form of the surfactant. Thus, it again appears that cis micelles are less effective than the trans aggregates at solubilizing the alkyl side chains of the HM-PAA, thereby resulting in a lower number of the polymer chains acting as bridges between the micelles. This phenomenon is similar to that observed in the crystal violet fluorescence studies, further suggesting a radical difference in the structure of trans and cis micelles. The relaxation time for the trans surfactant, determined as the inverse of the crossover frequency in Figure 6, exhibits a maximum at 15 mM, in accord with the trends shown in Figure 7.

Surface Tension of Dilute HM-PAA Solutions. The surface tension of 0.25 wt % HM-PAA/surfactant solutions is shown as a function of azoTAB concentration in Figure 8. This low value of the polymer concentration was chosen to avoid potential damage to the tensiometer that would arise upon submerging the platinum plate in high-viscosity gels. Even at very low surfactant concentrations the surface tension is significantly lower than that of pure water (72 mN/m), a result of the intrinsic surface activity of the polymer, owing to the amphiphilic nature of poly(acrylic acid) grafted with hydrophobic C_{12} side chains. At the lowest surfactant concentrations studied, the reduction in the surface tension is primarily a result of this HM-PAA surface activity. Surface activity measurements on a pure HM-PAA solution, or at surfactant concentrations lower than those reported in Figure 8, were not attempted because the equilibration times were too long (e.g., ~6 h at 0.083 mM), allowing for substantial undesired thermal cis → trans conversion during the experiments. The reason for this slow equilibration is that, in order to attain the equilibrium surface excess of adsorbed species, rearrangement and compression of the primary polymer layer is required,[70] which is a relatively slow process compared to that for the rearrangement of low molecular weight surfactant monolayers. The surface tension values obtained at the lowest surfactant concentration, however, agree well with the value of ca. 55 mN/m reported for HM-PAA (molecular weight = 120K g/mol, containing 3% substitution of C_{12} side chains) at a similar polymer concentration.[70]

An increase in the amount of cis or trans surfactant initially results in a slow decrease in the surface tension. This implies that newly added surfactant primarily binds to the polymer, since adsorption at the air−water interface would lead to a more rapid decrease in the surface tension. The slope of the surface tension plot at low surfactant concentrations is lower for the trans surfactant than the cis, indicating that the more hydrophobic trans form of the surfactant has a more favorable tendency to bind to the polymer. Conversely, the overall values of the surface tension are greater for the cis surfactant, which tends to bind less effectively to the polymer than does the trans form and has a lower propensity to adsorb at the air−water interface. The breakpoint at higher trans or cis surfactant concentrations at which the surface tension begins to decrease more strongly with concentration coincides with the cac values determined above for these photoisomers. Prior to the cac, the hydrophobic nature of the C_{12} side chains causes the HM-PAA to adsorb at the interface, as described above, despite the steric and conformational hindrances implicit in arranging the polyelectrolyte at the interface to allow the majority of the alkyl side chains to extend into the air, away from the water.[71] However, upon rapid micelle formation with increases in surfactant concentration beyond the cac, the free energy penalty associated with the strict polymer conformation required for adsorption at the air−water interface can be removed by solubilization of the side chains in the newly formed micelles. Thus, beyond the cac the amount of polymer adsorbed at the interface decreases dramatically as the surfactant concentration is increased, freeing up the interface for adsorption of surfactant. Since the surfactant can pack much more efficiently at the air−water interface than the polymer (about 60 Å^2 per surfactant molecule[5,72−74] vs 120 Å^2 per C_{12} side chain grafted to HM-PAA[70]), this provides for the rapid drop in surface tension beyond the cac observed in Figure 8. Phase separation occurs at surfactant concentrations above about 8 mM, similar to that observed beyond 50 mM for a polymer concentration of 2.5 wt %, again likely due to neutralization of the polymer−surfactant complex.

The results in Figure 8 can be contrasted with the well-known surface tension behavior observed in surfactant−polymer mixtures where the polymer is not hydrophobically modified. In the latter case, typically two break points are observed in plots of surface tension vs the log of concentration.[44,75] At low surfactant concentrations, the surface tension typically decreases rapidly with increases in surfactant concentration, similar to the behavior of pure surfactant solutions

below the cmc, implying that added surfactant primarily adsorbs at the interface as opposed to binding to the polymer. However, at a certain concentration T_1, the surface tension begins to decrease less rapidly with surfactant concentration, a clear indication of the onset of binding of the surfactant to the polymer. Thus, T_1 is typically equated to the cac value. Continued increases in the surfactant concentration cause the polymer to become saturated with the surfactant, and the surfactant monomer concentration eventually reaches the pure solution cmc value, leading to a second break point at concentration T_2. Beyond this concentration the surface tension reaches a constant value with the formation of normal (unbound) micelles. In the present case, however, hydrophobic interactions result in a gradual increase in surfactant binding with surfactant concentration even at very low amounts of surfactant,[76] in contrast to the case of traditional polymers where binding begins dramatically at the cac.

Conclusions

The photocontrolled aggregation of a photosensitive azobenzene surfactant onto an oppositely charged, hydrophobically modified polyelectrolyte results in photoreversible gelation. Surfactant micelles act as crosslinkers by solubilizing multiple alkyl side chains that are grafted onto adjacent polyelectrolyte molecules. The visible light (trans) form of the surfactant is more hydrophobic than the UV light (cis) form, and hence the trans form has a lower critical aggregation concentration (cac, i.e., the concentration where micelles first form in the presence of the polymer), resulting in the ability to photoinduce either micellization or demicellization. Rheology measurements indicate that reversible viscosity changes of up to 2 orders of magnitude can be realized. Fluorescence and absorbance measurements of the cationic probe crystal violet reveal an accelerated binding of the probe to sites near bound surfactant upon increasing the surfactant concentration up to the cac, while micelle formation beyond the cac causes the bound crystal violet to disassociate into solution due to wrapping of the polyelectrolyte around the charged micelles. Mixed-micelle formation between dodecyl chains and surfactant results in a gradual increase in the hydrophobic character of the solution as the azobenzene concentration is initially increased prior to the cac, with dynamic viscoelastic measurements revealing that the mixed micelles predominantly contain side chains from a single polymer molecule. Beyond the cac, however, cooperative binding gives rise to a rapid increase in the number of hydrophobic domains, with side chains from multiple polymer molecules being incorporated into a single micelle. A consistent picture is derived from all of the experimental techniques, indicating that the driving force for micellization at the cac is primarily an effect of hydrophobic interactions between surfactant tails, in contrast to electrostatic interactions between the polymer and the surfactant headgroup.

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